TURBINE COMPONENTS WITH THERMAL BARRIER COATINGS

CROSS-REFERENCE TO RELATED APPLICATION(S)

The present application is a continuation in part application of allowed U.S. Patent Application Serial No. 10/226,108 to Litton et al., filed August 21, 2002, entitled THERMAL BARRIER COATINGS WITH LOW THERMAL CONDUCTIVITY and a continuation in part application of U.S. Patent Application Serial No. 10/641,585 to Litton et al., filed August 12, 2003, entitled THERMAL BARRIER COATINGS WITH LOW THERMAL CONDUCTIVITY.

BACKGROUND OF THE INVENTION

The present invention relates to turbine components having a substrate formed from a ceramic material, such as a monolithic ceramic or a composite ceramic material, and a thermal barrier coating made from ceramic materials.

Gas turbine engines are well developed mechanisms for converting chemical potential energy, in the form of fuel, to thermal energy and then to mechanical energy for use in propelling aircraft, generating electrical power, pumping fluids, etc. At this time, the major available avenue for improved efficiency of gas turbine engines appears to be the use of higher operating temperatures. However, the metallic materials used in gas turbine engines are currently very near the upper limits of their thermal stability. In the hottest portion of modern gas turbine engines, metallic materials are used at gas temperatures above their melting points. They survive because they are air cooled. But providing air cooling reduces engine efficiency.

Accordingly, there has been extensive development of thermal barrier coatings for use with cooled gas turbine aircraft hardware. By using a thermal barrier coating, the amount of cooling air required can be substantially reduced,

thus providing a corresponding increase in efficiency.

Such coatings are invariably based on ceramic. Mullite and alumina have been proposed, but zirconia is the current material of choice. Zirconia must be modified with a stabilizer to prevent the formation of the monoclinic phase. Typical stabilizers include yttria, calcia, ceria, and magnesia.

Zirconia based ceramics are resistant to water attack. This is critical for land-based gas turbine applications, since the coatings are exposed at high temperatures for much longer than they are in aeroengine applications. Thus, corrosion of the thermal barrier coating can become a problem - indeed it is known to be a problem for silica-based thermal barrier coatings and alumina-based thermal barrier coatings. Steam is often injected into the combustor of land-based gas turbines to reduce nitric oxide formation, which exacerbates the water attack issue.

Despite the success with thermal barrier coatings, there is a continuing desire for improved coatings which exhibit superior thermal insulation capabilities, especially those improved in insulation capabilities when normalized for coating density. Weight is always a critical factor when designing gas turbine engines, particularly rotating parts. Ceramic thermal barrier coatings are not load supporting materials, and consequently they add weight without increasing strength. There is a strong desire for a ceramic thermal barrier material which adds the minimum weight while providing the maximum thermal insulation capability. In addition, there are the normal desires for long life, stability and economy.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a turbine component having a ceramic material substrate and a thermal barrier coating having low thermal

conductivity.

The foregoing object is attained by the turbine component of the present invention.

In accordance with the present invention, a turbine component is provided which broadly has a ceramic material substrate and a thermal barrier coating. The ceramic material substrate may be a monolithic ceramic material or a composite ceramic material. In a first embodiment of the present invention, the thermal barrier coating broadly comprises at least 15 mol% of at least one lanthanide sesquioxide and the balance comprising a first oxide selected from the group consisting of zirconia, ceria, and hafnia. The first oxide is preferably present in an amount greater than 50 mol%. The at least one lanthanide sesquioxide has a formula A_2O_3 where A is selected from the group consisting of La, Pr, Nd, Sm, Eu, Tb, and mixtures thereof.

In a second embodiment of the present invention, the thermal barrier coating broadly comprises greater than 30 mol% Sc_2O_3, a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Nd, Eu, Dy, Gd, Er, Pr, and mixtures thereof, and the balance zirconia.

In a third embodiment of the present invention, the thermal barrier coating broadly comprises more than 20 mol% In_2O_3, a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia.

In a fourth embodiment of the present invention, the thermal barrier coating broadly comprises from 5 to 60 mol% of at least one of La_2O_3 and Sm_2O_3, and from 5 to 60 mol% of at least one oxide having a formula A_2O_3 where A is selected from the group consisting of Sc, In, Y, Pr, nd, Eu, Gd, Dy, Er, Yb, and mixtures thereof, and the balance zirconia.

In a fifth embodiment of the present invention, the thermal barrier coating broadly comprises from 0.5 to 22.5

mol% of at least one first oxide having a formula A_2O_3 where A is selected from the group consisting of La, Sm, Tb, Tm, and Lu combined with a second oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a sixth embodiment of the present invention, the thermal barrier coating broadly comprises from 0.5 to 1.0 mol% of at least one first oxide from the group consisting of CeO_2, Pr_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, Y_2O_3, and mixtures thereof, combined with a second oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a seventh embodiment of the present invention, the thermal barrier coating broadly comprises 20.5 to 22.5 mol% of CeO_2 combined with an oxide selected from the group consisting of zirconia, hafnia, and ceria.

In an eighth embodiment of the present invention, the thermal barrier coating broadly comprises from 0.5 to 22.0 mol% of CeO_2, and from 0.5 to 22.0 mol% of at least one first oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, and mixtures thereof, combined with a second oxide selected from the group consisting of zirconia and hafnia. The CeO_2 and the at least one first oxide being present in an amount no greater than 22.5 mol%.

In a ninth embodiment, the thermal barrier coating broadly comprises from 0.5 to 22.5 mol% CeO_2, from 0.5 to 59.5 mol% of at least one oxide selected from the group consisting of In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia and hafnia.

In a tenth embodiment, the thermal barrier coating broadly comprises from 9.0 to 22.5 mol% of at least one first oxide selected from the group consisting of Pr_2O_3, Nd_2O_3, Eu_2O_3, Er_2O_3, and mixtures thereof, combined with a second oxide selected from the group consisting of zirconia, hafnia, and

ceria.

In an eleventh embodiment, the thermal barrier coating broadly comprises from 15.0 to 22.5 mol% of a first oxide selected from the group consisting of Dy_2O_3 and Yb_2O_3 combined with at least 77.5 mol% of a second oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a twelfth embodiment, the thermal barrier coating broadly comprises from 0.5 to 59.5 mol% of Dy_2O_3 and from 0.5 to 59.5 mol% of at least one oxide from the group consisting of In_2O_3, Sc_2O_3, MgO, CaO, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a thirteenth embodiment, the thermal barrier coating broadly comprises from 0.5 to 22.5 mol% of Yb_2O_3 and from 0.5 to 59.5 mol% of at least one oxide from the group consisting of In_2O_3, Sc_2O_3, MgO, CaO, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a fourteenth embodiment, the thermal barrier coating broadly comprises 20.5 to 60 mol% of at least one oxide selected from the group consisting of In_2O_3, Sc_2O_3, MgO, CaO, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a fifteenth embodiment, the thermal barrier coating broadly comprises from 15 to 59.5 mol% of Y_2O_3, from 0.5 to 45.0 mol% of at least one first oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

In a sixteenth embodiment, the thermal barrier coating broadly comprises from 9.0 to 23.0 mol% Gd_2O_3, from 0.5 to 51.0 mol% of at least one first oxide selected from the group

consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

Other details of the turbine components with thermal barrier coatings of the present invention, as well as other objects and advantages attendant thereto, are set forth in the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The essence of the present invention arises from the discovery that certain ceramic materials have great utility as thermal barrier coatings on ceramic material substrates, particularly those used to form components, such as the airfoils, of turbine engine components. These ceramic coating materials have such utility because they exhibit lower thermal conductivity that conventional thermal barrier coatings such as 7 weight% yttria stabilized zirconia.

In accordance with the present invention, a first embodiment of a thermal barrier coating which exhibits such a lower thermal conductivity comprises at least 15 mol% of at least one lanthanide sesquioxide and the balance comprising a first oxide selected from the group consisting of zirconia, ceria, and hafnia. Preferably, the first oxide is present in an amount greater than 50 mol%. Each lanthanide sesquioxide has a formula A_2O_3 where A is selected from the group consisting of La, Pr, Nd, Sm, Eu, Tb, and mixtures thereof. In a preferred embodiment, the at least one lanthanide sesquioxide is present in a total amount in the range of 15 to 45 mol%. In a most preferred embodiment, the at least one lanthanide sesquioxide is present in a total amount of at least 25 mol%. In the thermal barrier coatings of the present invention, where the first oxide is zirconia, each zirconium ion has more than one adjacent oxide vacancy on average, and

preferably at least two adjacent oxide vacancies. If the first oxide is hafnia or ceria, each hafnium ion and each cerium ion would also have more than one adjacent oxide vacancy on average, and preferably at least two adjacent oxide vacancies. The presence of these oxygen vacancies minimizes the thermal conductivity of the coating. Thus, they are a highly desirable feature of the coatings of the present invention.

A second thermal barrier coating in accordance with the present invention comprises a lanthanide sesquioxide present in an amount from 5 to 60 mol% and the balance comprising a first oxide selected from the group consisting of zirconia, hafnia, and ceria. The lanthanide sesquioxide has a formula A_2O_3 where A is selected from the group consisting of In, Sc, Y, Dy, Ho, Er, Tm, Yb, Lu, and mixtures thereof. In a preferred embodiment of this coating, the lanthanide sesquioxide is present in an amount from 10 to 40 mol%.

A third embodiment of a thermal barrier coating comprises a lanthanide sesquioxide and the balance comprising a first oxide selected from the group consisting of zirconia, hafnia, ceria, and mixtures thereof. The lanthanide sesquioxide is present in an amount sufficient to create more than one oxygen vacancy on average adjacent each zirconium, hafnium, and cerium ions.

A fourth embodiment of a thermal barrier coating having a lower thermal conductivity in accordance with the present invention comprises from 15 to 60 mol% of a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Yb, Eu, Dy, Pr, Sm, La, and mixtures thereof, and the balance zirconia. The thermal barrier coating preferably contains less than 10 vol% of phases with a pyrochlore crystal structure. Zirconia is preferably present in an amount greater than 40 mol%. The thermal barrier coating may also contain one or more of the following constituents: from 0.001 to 2.5 mol% yttria, from

0.001 to 10 mol% of at least one of CaO and MgO, from 0.001 to 1.0 mol% Yb_2O_3, from 0.001 to 4.0 mol% Sc_2O_3, and/or from 0.001 to 4.0 mol% In_2O_3.

A fifth embodiment of a thermal barrier coating in accordance with the present invention which exhibits a lower thermal conductivity comprises at least 15 mol% yttria, and a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Yb, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. In a preferred embodiment, the zirconia is present in an amount greater than 40 mol% and the coating contains less than 10 vol% of phases with a pyrochlore crystal structure. The yttria in this coating system may be present in an amount in the range of 15 to 22 mol% and the lanthanide sesquioxide may be present in an amount from 1.0 to 35 mol%. In a particularly useful embodiment of this thermal barrier coating system, yttria is present in an amount greater than 22 mol% and the lanthanide sesquioxide is present in an amount from 1.0 to 38 mol%.

In a sixth embodiment of the present invention, a thermal barrier coating having a lower thermal conductivity comprises from 9 to 15 mol% Yb_2O_3, and from 1.0 to 48 mol% of a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. The zirconia is present in an amount greater than 40 mol% and the coating has less than 10 vol% of a pyrochlore crystal structure.

A seventh embodiment of a thermal barrier coating in accordance with the present invention comprises greater than 15 mol% Yb_2O_3 and a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. The zirconia is preferably present in an amount greater than 40 mol%. Further, the coating preferably contains less than 10

vol% of phases with a pyrochlore crystal structure. The lanthanide sesquioxide may be present in an amount from 0.001 to 45 mol%.

In an eighth embodiment of the present invention, a thermal barrier coating is provided which comprises from 20 to 30 mol% Sc_2O_3 and a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. As before, the zirconia is preferably present in an amount greater than 40 mol%. Further, the thermal barrier coating has less than 10 vol% of phases with a pyrochlore crystal structure. In a preferred embodiment, the lanthanide sesquioxide is present in an amount from 0.001 to 30 mol%.

In a ninth embodiment of the present invention, a thermal barrier coating is provided which comprises greater than 30 mol% Sc_2O_3, a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Nd, Eu, Dy, Gd, Er, Pr, and mixtures thereof, and the balance zirconia. The zirconia is preferably present in an amount greater than 40 mol%. The thermal barrier coating may have less than 10 vol% of phases with a pyrochlore crystal structure. In a preferred embodiment, the lanthanide sesquioxide is present in an amount in the range of 0.001 to 30 mol%.

In a tenth embodiment of the present invention, a thermal barrier coating comprises from 11 to 20 mol% In_2O_3 and a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. In a preferred embodiment, the lanthanide sesquioxide is present in an amount from 0.001 to 36 mol%. The zirconia is preferably present in an amount greater than 40 mol%. The coating also preferably contains less than 10 vol% of phases with a pyrochlore structure.

In an eleventh embodiment, a thermal barrier coating is

provided which comprises more than 20 mol% In_2O_3, and a lanthanide sesquioxide having a formula A_2O_3 where A is selected from the group consisting of Er, Nd, Eu, Dy, Gd, Pr, and mixtures thereof, and the balance zirconia. In this coating system, the zirconia is preferably present in an amount greater than 40 mol%, the lanthanide sesquioxide is preferably present in an amount from 0.001 to 40 mol%, and the coating contains less than 10 vol% of phases with a pyrochlore structure.

In a twelfth embodiment of the present invention, a thermal barrier coating comprises from 5 to 60 mol% of at least one of La_2O_3 and Sm_2O_3, from 5 to 60 mol% of at least one oxide having the formula A_2O_3 where A is selected from the group consisting of Sc, In, Y, Pr, Nd, Eu, Sm, Gd, Dy, Er, Yb, and mixtures thereof, and the balance zirconia. In this coating system, the zirconia is preferably present in an amount greater than 40 mol% and the coating contains less than 10 vol% of phases with a pyrochlore structure.

Other embodiments of thermal barrier coatings in accordance with the present invention include the following:

A thermal barrier coating comprising from 0.5 to 22.5 mol% of at least one first oxide having a formula A_2O_3 where A is selected from the group consisting of La, Sm, Tb, Tm, and Lu combined with a second oxide selected from the group consisting of zirconia, hafnia, and ceria. In a preferred embodiment, the second oxide is present in an amount of at least 77.5 mol%. The coating may also contain from 0.5 to 59.5 mol% of at least one third oxide from the group consisting of In_2O_3, Sc_2O_3, Y_2O_3, MgO, CaO, and mixtures thereof with the second oxide being present in an amount greater than 40 mol% when the third oxide is present. Still further, the coating, in another variation, may contain from 0.5 to 22.5 mol% of at least one third oxide selected from the group consisting of CeO_2, Pr_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, and mixtures

thereof, and trhe at least one first oxide and the at least one third oxide being present in a total content no greater than 22.5 mol%.

A thermal barrier coating comprising from 0.5 to 1.0 mol% of at least one first oxide from the group consisting of CeO_2, Pr_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, Y_2O_3, and mixtures thereof, combined with a second oxide selected from the group consisting of zirconia, hafnia, and ceria. The thermal barrier coating may also contain from 0.5 to 22.5 mol% of at least one third oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, and mixtures thereof, with the at least one first oxide and the at least one third oxide being present in a total amount of no greater than 22.5 mol%, and the second oxide being present in an amount of at least 77.5 mol%.

A thermal barrier coating comprising from 20.5 to 22.5 mol% of CeO_2 combined with an oxide selected from the group consisting of zirconia and hafnia. In a preferred embodiment, the oxide is present in an amount of at least 77.5 mol%.

A thermal barrier coating comprising from 0.5 to 22.0 mol% of CeO_2, and from 0.5 to 22.0 mol% of at least one first oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, and mixtures thereof, combined with a second oxide selected from the group consisting of zirconia and hafnia, and the CeO_2 and the at least one first oxide being present in an amount no greater than 22.5 mol%. In a preferred embodiment, the second oxide is present in an amount of at least 77.5 mol%.

A thermal barrier coating comprising from 0.5 to 22.5 mol% CeO_2, from 0.5 to 59.5 mol% of at least one oxide selected from the group consisting of In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia and hafnia.

A thermal barrier coating comprising from 9.0 to 22.5 mol% of at least one first oxide selected from the group consisting of Pr_2O_3, Nd_2O_3, Eu_2O_3, Er_2O_3, and mixtures thereof combined with a second oxide selected from the group consisting of zirconia, hafnia, and ceria. In a preferred embodiment, the second oxide is present in an amount greater than 77.5 mol%. The thermal barrier coating may further comprise from 0.5 to 51.0 mol% of at least one third oxide selected from the group consisting of Yb_2O_3, In_2O_3, Sc_2O_3, Y_2O_3, Gd_2O_3, MgO, CaO, and mixtures thereof with the second oxide being present in an amount of at least 40 mol%.

A thermal barrier coating comprising from 15.0 to 22.5 mol% of a first oxide selected from the group consisting of Dy_2O_3 and Yb_2O_3 combined with at least 77.5 mol% of a second oxide selected from the group consisting of zirconia, hafnia, and ceria.

A thermal barrier coating comprising from 0.5 to 59.5 mol% of Dy_2O_3 and from 0.5 to 59.5 mol% of at least one oxide from the group consisting of In_2O_3, Sc_2O_3, MgO, CaO, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

A thermal barrier coating comprising from 0.5 to 22.5 mol% of Yb_2O_3, and from 0.5 to 59.5 mol% of at least one oxide from the group consisting of In_2O_3, Sc_2O_3, MgO, CaO, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

A thermal barrier coating comprising from 20.5 to 60 mol% of at least one oxide selected from the group consisting of In_2O_3, Sc_2O_3, and Y_2O_3, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

A thermal barrier coating comprising from 15 to 59.5 mol%

of Y_2O_3, from 0.5 to 45.0 mol% of at least one first oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

A thermal barrier coating comprising from 9.0 to 23.0 mol% Gd_2O_3, from 0.5 to 51.0 mol% of at least one first oxide selected from the group consisting of La_2O_3, Sm_2O_3, Tb_2O_3, Tm_2O_3, Ho_2O_3, Lu_2O_3, MgO, CaO, Pr_2O_3, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3, In_2O_3, Sc_2O_3, and mixtures thereof, combined with at least 40 mol% of an oxide selected from the group consisting of zirconia, hafnia, and ceria.

The various thermal barrier coatings set forth herein may be characterized with a columnar structure.

An article, having particular utility as a component in a gas turbine engine, may be provided in accordance with the present invention. The article may have a metal substrate and one of the aforementioned thermal barrier coatings applied to the substrate. The thermal barrier coating may be applied directly to a surface of the substrate or may be applied to a bond coat deposited on one or more surfaces of the metal substrate. Any suitable technique known in the art may be used to deposit a thermal barrier coating in accordance with one of the embodiments of the present invention. Suitable techniques include electron beam physical vapor deposition, chemical vapor deposition, LPPS techniques, and diffusion processes. The metal substrate may comprise one of a nickel based superalloy, a cobalt based superalloy, a ferrous alloy such as steel, a titanium alloy, and a copper alloy.

In lieu of a metal substrate, the turbine component or article may have a substrate formed from ceramic material such as a monolithic ceramic material or a composite ceramic material. As used herein, the term "monolithic ceramic" is

meant to include, but is not limited to, single-phase or multi-phase ceramics, but not ceramics processed as composites (i.e. infiltrated fiber weaves, etc.). Examples of monolithic ceramic substrates include, but are not limited to, silicon nitride and also self-reinforced silicon nitride. Examples of composite ceramic substrates include, but are not limited to, SiC-SiC composites (vapor- or melt-infiltrated 2D or 3D fiber weaves) and C - C composites (again, vapor- or melt-infiltrated 2D or 3D fiber weaves).

When a bond coat is used, the bond coat may comprise any suitable bond coat known in the art. For example, the bond coat may be formed from an aluminum containing material, an aluminide, a platinum aluminide, a ceramic material, such as 7wt% yttria stabilized zirconia, or a MCrAlY material. Alternatively, the bond coat may be multiple layers of ceramics which are designed to provide coefficient of thermal expansion match as well as to provide oxidation resistance (by blocking oxidation diffusion) and corrosion resistance (by blocking corrosive oxide liquid attack). Suitable bond coats may be formed from Ta_2O_5, all rare-earth disilicates having the formula $X_2Si_2O_7$ where X = La, Nd, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and mixtures thereof, $Y_2Si_2O_7$, mullite, BSAS (barium strontium alumino silicate or celsian), yttrium aluminum garnet, ytterbium aluminum garnet, and other rare-earth aluminate garents where the rare earth element is selected from the group consisting of Gd, Tb, Dy, Ho, Er, Tm, Lu, and mixtures thereof. The multiple bond coat layers may be multiple distinct layers formed from the same or different materials. Additionally, the multiple bond coat layers may be functionally graded layers of mixtures of the above. In addition to serving as matching layers and bond coat layers, these layers act as environment barriers and oxygen barriers. Functional grading may be used to replace a distinct interface between two layers of dissimilar materials with a region in

which the two materials are mixed such that the overall concentration gradually changes from 100% of the first material to 100% of the second material. Thus, a step change in concentration may be replaced with a gradually sloping change in concentration. This approach is effective in reducing residual stresses, for example between layers of materials with large thermal expansion mismatches.

The bond coat may be formed on the substrate, metallic or ceramic, using any suitable process known in the art including, but not limited to, low pressure plasma spray, electron beam physical vapor deposition, diffusion processes and chemical vapor deposition processes. If desired, the bond coat may have an oxide scale on an outer surface, which oxide scale consists essentially of alumina. The thermal barrier coatings of the present invention may be bonded to the oxide scale using any suitable technique known in the art.

If desired, a ceramic layer may be bonded to the thermal barrier coating. The additional ceramic material may be selected from the group consisting of materials which reduce oxygen diffusion, provide erosion and abrasion resistance, and/or provide optical emissivity of 0.7. Examples of high emissivity ceramic materials which can be used are alumina and mullite. High emissivity reduces the heat transfer across a thermal barrier coating by internal radiation (radiation of the thermal barrier coating material itself) due to the temperature difference between the hotter outer surface of the coating and the cooler interface between the coating and the TGO, thereby reducing the temperature of the TGO, thus the bondcoat, thus the alloy. Thus, high emissivity increases the insulative properties of the TBC. The additional ceramic layer may be formed over an exterior surface of the thermal barrier coating.

In some embodiments, the article may have an oxide scale on its surfaces and one of the thermal barrier coatings of the

present invention may be applied directly over and bonded to the oxide scale using any suitable deposition technique known in the art including, but not limited to, diffusion processes, electron beam physical vapor deposition, and/or chemical vapor deposition techniques. The oxide scale may consist substantially of alumina.

Although the thermal barrier coatings of the present invention were developed for application in gas turbine engines, the coatings have utility in other applications where high temperatures are encountered, such as furnaces and internal combustion engines.

The following examples are intended to show the advantages of the coatings of the present invention.

EXAMPLE 1

Samples of 27.3 mole% Y_2O_3, balance ZrO_2, were produced by cold pressing and sintering of mixed powders to a density 95% of theoretical. The sample discs, 0.025" in thickness, were coated with graphite. Specific heat and thermal diffusivity measurements were made using the laser flash apparatus. Bulk density was determined by careful measurement of the sample dimensions and weight. Thermal conductivity values of 1.95 W/mK were calculated from the data measured at 1200°F, linearly corrected to theoretical density.

EXAMPLE 2

Samples of 16.7 mole% Y_2O_3, 16.7 mole% Gd_2O_3, balance ZrO_2, were similarly produced by cold pressing and sintering of mixed powders to a density 90.8% of theoretical. The 0.025"-thick samples were again coated with graphite and measured in the laser flash apparatus. From careful measurements of sample weight and dimensions, the bulk density of the sample was determined. Thermal conductivity values averaging 1.37 W/mK were calculated from the data measured at 1600°F, linearly

corrected to theoretical density.

EXAMPLE 3

Coatings with an average composition of 19 mole% Sm_2O_3, balance ZrO_2, were deposited by electron beam physical vapor deposition onto alumina discs. High temperature measurements of thermal diffusivity were made in the laser flash apparatus. High temperature specific heat values were estimated from previous measurements of monolithic 33 mole% Sm_2O_3, balance ZrO_2 samples. Bulk density of the samples was calculated from the changes in weight and thickness of the discs during coating, and their diameters. Thermal conductivity values averaging 1.26 W/mK were calculated from the data measured at 1400°F, with no correction made for density.

It is apparent that there has been provided in accordance with the present invention thermal barrier coatings having low thermal conductivity which fully satisfy the objects, means, and advantages set forth hereinbefore. While the present invention has been described in the context of specific embodiments thereof, other alternatives, modifications, and variations will become apparent to those skilled in the art having read the foregoing description. Accordingly, it is intended to embrace those alternatives, modifications, and variations as fall within the broad scope of the appended claims.